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# SYNTHESIS OF SILVER/COPPER NANOPARTICLES AND THEIR METAL-METAL BONDING PROPERTY

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***Abstract***

*The present paper describes a metal-metal bonding technique using Cu nanoparticles containing Ag nanoparticles (Ag/Cu nanoparticles). The Ag/Cu nanoparticles with particle sizes of 30-85 nm and crystal sizes of 9.3 nm for Cu and 8.1 nm for Ag were produced by reducing $5.0\times10^{-3}$ M $Ag^{+}$ ($AgClO_4$) and $5.0\times10^{-3}$ M $Cu^{2+}$ ($Cu(NO_3)_2$) simultaneously with 1.0 M hydrazine in aqueous solution containing 1.0 g/L poly(vinylpyrrolidone) as dispersing agent and $5\times10^{-3}$ M citric acid as stabilizer at room temperature. Discs of metallic Cu or metallic Ag were successfully bonded under annealing at 400°C and pressurizing at 1.2 MPa for 5 min in $H_2$ gas with help of the Ag/Cu particles. The shear strengths required for separating the bonded discs were as large as 19.7 for the Cu discs and 16.0 MPa for the Ag discs .*

**Keywords:** *Nanoparticles; Copper; Silver; Filler; Metal-metal bonding.*

## 1. Introduction

A bonding technique is quite required for connecting solid state materials, especially in civil engineering, construction industry and electronics [1]. For a process of bonding of metallic materials, annealing of the materials to be bonded are usually performed [2, 3]. In this process, their components diffuse near their interface, which results in metal-metal bonding. Inserting of metallic powders between the metallic materials as the filler may help the bonding, because the metallic powders melt and diffuse into the metallic materials during pressed under annealing. Nano-sized metallic particles are desired as the filler, since their melting points decrease with a decrease in their size [4-6], and consequently the metal-metal bonding can be performed at low temperatures. From this view point, nanoparticles of metal have been examined for the bonding [7-10]. Among metallic particles, metallic copper (Cu) particles are promising as the filler in metal-metal bonding, because they do not take cost. However, they are easily oxidized in atmosphere of air [11,12], which spoils bonding properties. To solve the problem, our group developed a preparation method of chemically-stable Cu particles, in which the particles were produced by reducing $Cu^{2+}$ in the presence of stabilizer [13,14], or by reducing copper oxide nanoparticles prepared by metal salt-base reaction in aqueous solution [15], and revealed strong bonding of metallic copper. Apart from the Cu nanoparticles, our group also have studied on metal-metal bonding process using the copper oxide nanoparticles, in which reduction of copper oxide to metallic copper and Cu-Cu bonding took place simultaneously [16].

In a preliminary experiment, Cu nanoparticles could be used as the filler for bonding metallic silver. However, the bonding strength was not as large as that in the case of metallic silver (Ag) nanoparticles. The nanoparticles of metal that is the same kind of metal as the materials are suitable for bonding metallic materials, due to the fit of d-values of the particles and the materials. Accordingly, Cu nanoparticles containing Ag nanoparticles (Ag/Cu nanoparticles) will function as almighty filler for bonding of metallic copper and metallic silver, and the use of the Ag/Cu nanoparticles contributes to lowering of cost. In our previous work [17], mixture of copper oxide nanoparticles and silver oxide nanoparticles was examined for bonding of not only metallic copper but also metallic silver. Though this bonding process worked well, the mixture had to be fabricated with many steps composed of synthesis of copper oxide nanoparticles, synthesis of silver oxide nanoparticles, and homogeneously-mixing of those nanoparticles.

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In the present work, we propose a method for producing Ag/Cu nanoparticles for metal-metal bonding process. The Ag/Cu nanoparticles were prepared by only one step, *i.e.*, by reducing $Ag^+$ and $Cu^{2+}$ simultaneously with hydrazine in aqueous solution. This preparation method was quite simple because of the preparation by one step. Their bonding properties were also studied.

## 2. Experimental

### 2.1 Materials

Silver perchlorate ($AgClO_4$) (>99.0%) and copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) (77.0-80.0 %, as $Cu(NO_3)_2$) were used as precursors of Ag and Cu, respectively. Polyvinylpyrrolidone (PVP) (K-30 (Mw=40000)) was used as a dispersing agent in preparation of nanoparticles. Citric acid monohydrate (>99.5%) was used as an agent that chemically stabilizes Cu nanoparticles. Hydrazine monohydrate (>98.0%) was used as a reducing reagent for metal ions. All chemicals were purchased from Kanto Chemical Co., Inc., and were used as received. Water that was ion-exchanged and distilled with Shimadzu SWAC-500 was used in all the preparations, and was deaerated by bubbling with $N_2$ gas for 30 min prior to preparation of aqueous solutions.

### 2.2 Preparation

Figure 1 shows a procedure for preparing Ag/Cu nanoparticle colloid solution. The particle colloid solution was prepared by mixing of $AgClO_4$, $Cu(NO_3)_2$ and hydrazine. Hydrazine was added to aqueous solution containing $AgClO_4$, $Cu(NO_3)_2$, PVP and citric acid under vigorous stirring at room temperature. Initial concentrations of $AgClO_4$, $Cu(NO_3)_2$, PVP, citric acid and hydrazine were $5.0\times10^{-3}$ M, $5.0\times10^{-3}$ M, 1.0 g/L, $5\times10^{-3}$ M and 1.0 M, respectively. The reaction time was 3 h. A dark-red and muddy colloid solution was produced. A Cu nanoparticle colloid solution was also prepared by the same method, except initial concentrations of $AgClO_4$ and $Cu(NO_3)_2$ were 0 and $1.0\times10^{-2}$ M, respectively.

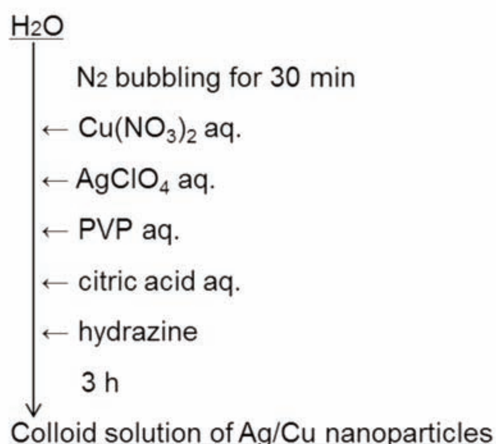


***Figure 1.*** *Procedure for preparing colloid solution of Ag/Cu nanoparticles.*

### 2.3 Apparatus and Procedures

The particles were characterized by transmission electron microscopy (TEM) and X-ray diffractiometry (XRD). TEM was performed with a JEOL JEM-2000FX II microscope operating at 200 kV. Samples for TEM were prepared by dropping and evaporating the particle colloid solution on a collodion-coated copper grid. XRD measurements were carried out with a Rigaku RAD-B X-ray diffractometer at 50 kV and 150 mA with $CuK\alpha_1$ radiation. For preparing powder samples for the XRD measurements, supernatant of the particle colloid solution was removed with decantation, and then residue of the colloid solution was dried at room temperature for 24 h in vacuum.

Bonding property was investigated with a set-up used in our previous works [13,14]. The powder samples, obtained in the same procedure as used for the XRD measurements, were sandwiched between a large disc (diameter: 10 mm, thickness: 5 mm) and a small disc (diameter: 5 mm, thickness: 2.5 mm), and pressed under annealing at 400$^o$C in $H_2$ gas at 1.2 MPa for 5 min. The discs used were made of metallic copper (Cu discs), and Cu discs, of which surfaces were plated with metallic silver (Ag discs). After the bonding, shear strength required for separating the bonded discs was measured. The disc surfaces were characterized by scanning electron microscopy (SEM) after the measurements of shear strengths. SEM was performed with a JEOL JSM-5600LV microscope.

## 3. Results and Discussion

### 3.1 Ag/Cu nanoparticles

In our previous works employing fabrication Cu nanoparticles [13, 14], copper chloride was used as one of starting chemicals for producing Cu nanoparticles. The present work used not copper chloride but $Cu(NO_3)_2 \cdot 3H_2O$ for producing Ag/Cu nanoparticles, because $Ag^+$ forms white precipitate of AgCl with $Cl^-$. Cetyltrimethylammonium bromide (CTAB), which was used as a dispersing agent for producing Cu nanoparticles in the previous works [13, 14], contains $Br^-$. Since $Ag^+$ forms yellowish precipitate of AgBr with $Br^-$, CTAB could not be used in the present work, either. PVP is often used as a stabilizer for metallic nanoparticles. Accordingly, PVP was used instead of CTAB in the present work.

Figure 2 (a) shows a TEM image of Cu particles,

which did not contain Ag. Particles with a size of ca. 100 nm were produced, and the particles formed aggregates. Figure 3 (a) shows a XRD pattern of Cu particles. The peaks, appeared clearly at 43.3, 50.4 and 74.1 degree, were attributed to the (110), (111), and (200) reflections of cubic metallic copper (JCPDS card No. 4-0836), respectively. Their average crystal size was estimated from X-ray diffraction line broadening of the (111) peak according to the Scherrer equation; the size was 49.7 nm. Figure 2 (b) shows a TEM image of Ag/Cu particles. Produced particles had sizes of 30-85 nm, and also formed aggregates. The particle sizes were smaller than that for the Cu particles with no Ag. The solution in the case of production of Ag/Cu particles became dark-red and muddy faster after the hydrazine addition comparing to the Cu particles production, though a mechanism for the difference in reaction rate is not clear. Many nuclei were generated in the fast reaction, which resulted in production of many particles with the small size. Figure 3 (b) shows an XRD pattern of Ag/Cu particles. Besides the peaks due to cubic metallic copper, peaks were recorded at 38.1, 64.8 and 77.6. They were assigned to the (111), (220), and (311) reflections of cubic metallic silver (JCPDS card No. 4-0783), respectively. This result indicated that reduction of both $Ag^+$ and $Cu^{2+}$ could be made with the present method. The metallic copper peak position did not change compared to those for the Cu particles. Accordingly, no alloy of Ag and Cu, but mixture or aggregates of the Ag particles and the Cu particles were produced. Their crystal sizes of Cu and Ag were estimated by applying the Scherrer equation to the (111) cubic metallic copper peak and the (111) cubic metallic silver peak, respectively. The sizes were 9.3 nm for Cu and 8.1 nm for Ag. The sizes of particles and crystals were smaller those that for the Cu nanoparticles (49.7 nm), respectively, though a mechanism for the difference is still unclear.

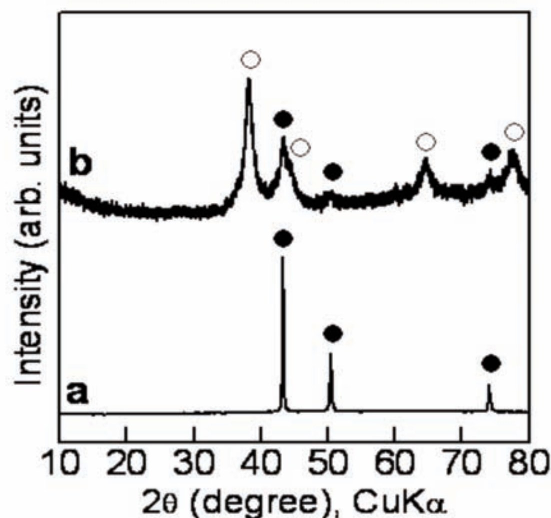


***Figure 3.*** *XRD patterns of Cu nanoparticles (a) and Ag/Cu nanoparticles (b). ●: cubic metallic copper, ○: cubic metallic silver.*

### *3.2 Bonding property for Cu discs (Cu-Cu bonding property)*

Figure 4 shows photographs of large Cu discs after measurement of shear strength. The surfaces for both the Cu nanoparticles and the Ag/Cu nanoparticles were brown. The brown surfaces appeared to be derived from bulk of metallic copper. This observation implied that both nanoparticles were not oxidized, and contributed to Cu-Cu bonding. Shear strengths of nanoparticles for the Cu discs are shown in Table 1. Shear strengths were 21.8 and 19.7 MPa with the use of the Cu particles and the Ag/Cu particles, respectively. There was no large difference in the shear strength between the particles. Since there is a mismatch of d-value between Cu and Ag, Ag cannot assist to Cu-Cu bonding efficiently.

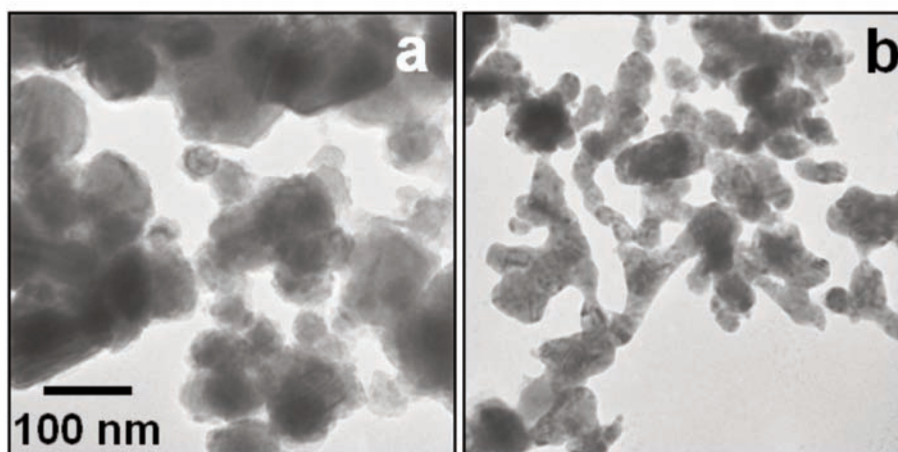


***Figure 2.*** *TEM images of Cu nanoparticles (a) and Ag/Cu nanoparticles (b).*

Nevertheless, the high shear strength equivalent to the Cu particles was given for the Ag/Cu particles. The Au/Cu particles had the small particle size and the crystal sizes, compared to the Cu particles, as given in the previous section. Smooth diffusion of the small particles into the metallic surfaces probably took place, since small particles have a low melting point [4-6]. Consequently, the discs were strongly bonded. Figure 5 shows SEM images of the Cu disc surfaces after measurement of shear strength. Sintering of the particles was observed for both the particles, which was evidence of the strong bonding.

### *3.3 Bonding property for Ag discs (Ag-Ag bonding property)*

Figure 6 shows photographs of large Ag discs after measurement of shear strength. The surfaces for both nanoparticles were brown, which appeared to be due to bulk of metallic copper. This observation also

***Table 1.*** *Shear strengths of nanoparticles for metallic discs.*

| filler \ disc | Cu discs | Ag discs |
|---|---|---|
| Cu nanoparticles | 21.8 | 11.3 |
| Ag/Cu nanoparticles | 19.7 | 16.0 |

units: MPa

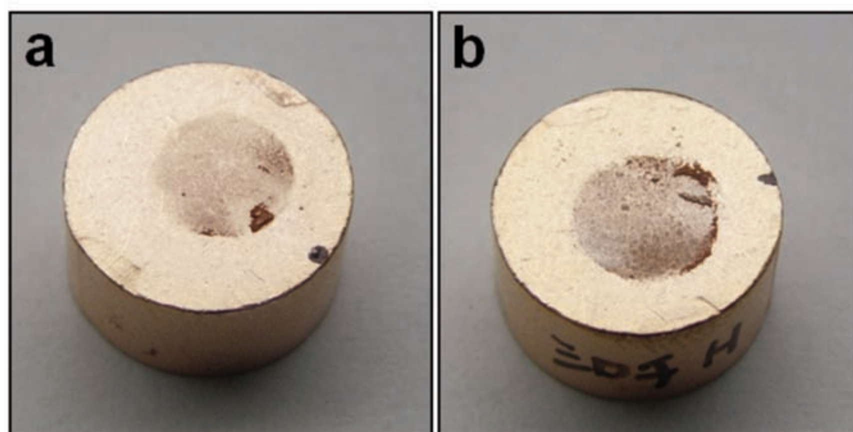


***Figure 4.*** *Photographs of Cu discs after measurements of shear strengths. The particles used were (a) Cu nanoparticles and (b) Ag/Cu nanoparticles.*

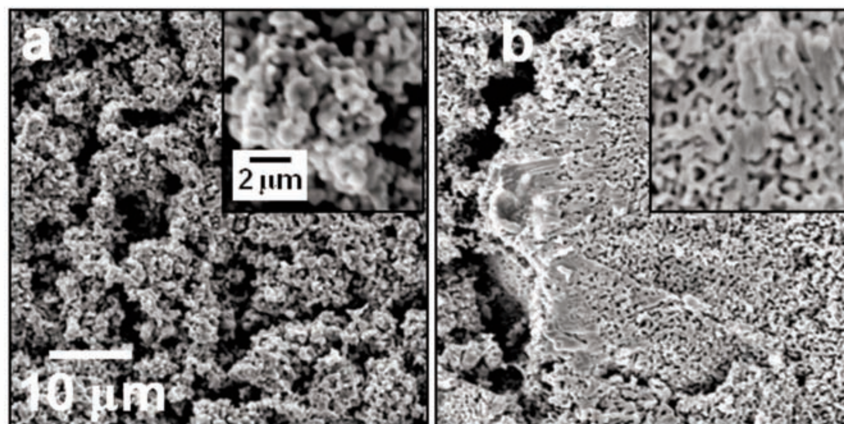


***Figure 5.*** *SEM images of Cu disc surfaces after measurements of shear strengths. The particles used were (a) Cu nanoparticles and (b) Ag/Cu nanoparticles.*

implied that the Cu nanoparticles helped Ag-Ag bonding. However, contribution of the Ag nanoparticles to bonding was not clearly confirmed with the photograph, because the surfaces were not silvery white. Shear strengths of nanoparticles for Ag discs are also shown in Table 1. With the respect to the Cu particles, shear strength was as low as 11.3 MPa, though the Ag discs were successfully bonded. Since there is a mismatch of d-value between Cu and Ag, the low shear strength was given. In contrast, a shear strength was achieved 16.0 MPa by using the Ag/Cu particles. The Ag contained in the Ag/Cu particles diffused smoothly into the Ag surfaces, which resulted in the strong Ag-Ag bonding. Another possible mechanism on the strong bonding could be considered in a way similar to the Cu-Cu bonding, as follows. The Au/Cu particles diffused smoothly into the metallic surfaces because of their small sizes, which resulted in the strong bonding. Figure 7 shows SEM images of the Ag disc surfaces after measurement of shear strength. Sintering of the particles took place for both the particles as well as in the case of the Cu discs. Accordingly, the bonding for the Ag discs was strongly performed with the use of the Ag/Cu particles.

## 4. Conclusion

The metal-metal bonding by the use of Ag/Cu nanoparticles was performed in the present work. The Ag/Cu nanoparticles helped the bonding not only for the Cu discs but also for the Ag discs, between which the particles were pressed under annealing at 400$^{o}$C in $H_2$ gas at 1.2 MPa. The shear strengths required for separating the bonded discs recorded for the Cu discs and the Ag discs were as large as 19.7 and 16.0 MPa, respectively.

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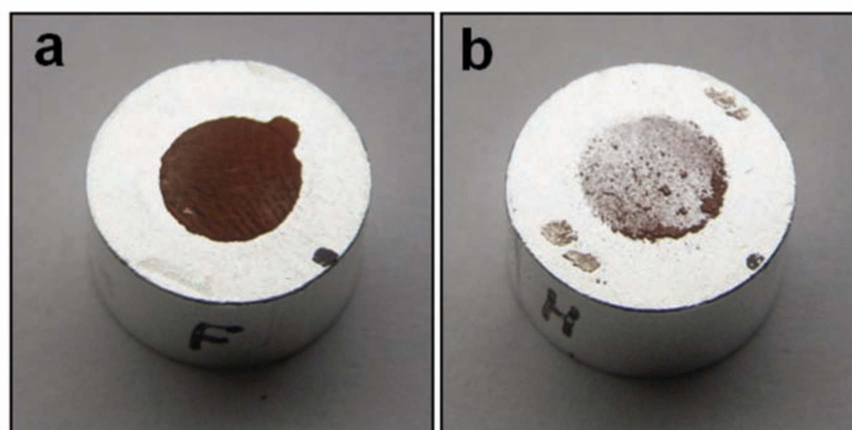


***Figure 6.*** *Photographs of Ag discs after measurements of shear strengths. The particles used were (a) Cu nanoparticles and (b) Ag/Cu nanoparticles.*

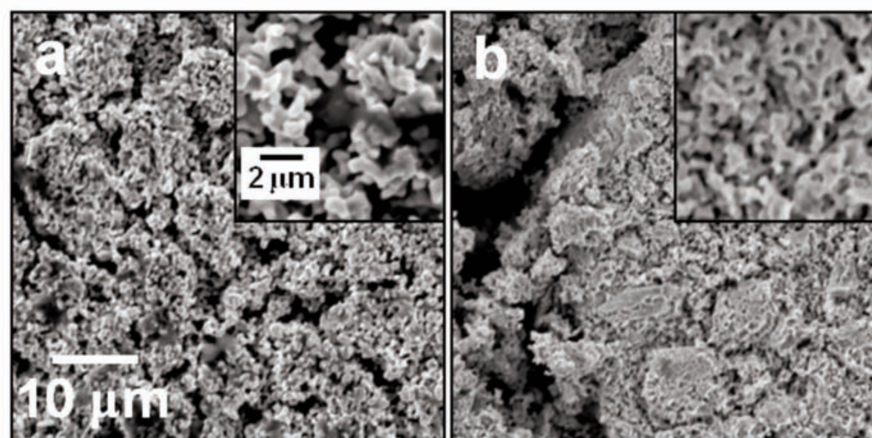


***Figure 7.*** *SEM images of Ag disc surfaces after measurements of shear strengths. The particles used were (a) Cu nanoparticles and (b) Ag/Cu nanoparticles.*

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